The Estimation of Pentoses and Pentosans

I—The Formation and Distillation of Furfural.
II—The Determination of Furfural.

A THESIS SUBMITTED TO THE FACULTY OF THE GRADUATE SCHOOL OF THE UNIVERSITY OF MINNESOTA

BY

NORVILLE CLARENCE PERVIER

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

JUNE, 1922

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NORVILLE C. PERVIER

The Estimation of Pentoses and Pentosans[1]

By Norville C. Pervier

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I—The Formation and Distillation of Furfural

Following a review of previous work on the formation of furfural, Part I is a study of the factors influencing the production of furfural from pure arabinose, pure xylose, gum arabic, and pine sawdust. A method for distilling pentoses from acid solution by steam is described, in which theoretical yields of furfural are discussed.

Part II, describes several new volumetric methods for the determination of furfural in aqueous solution, and includes a bibliography on pentoses and pentosans.

THAT the wide distribution of the pentosans in nature, as pointed out by Tollens in 1891, may be of considerable significance in plant economy, is indicated by the work of Spoehr, Hooker, and Rosa. These substances also constitude a large portion of the nitrogen-free extract of many animal feeds and have been the subject of numerous experiments in animal metabolism. (McCollum and Brannon, Swartz.) The pentosan determination has also been used as a basis for determining the degree of milling of flours (Gerum). It is apparent, then, that a convenient and accurate method for estimating these substances is very necessary. Because of the serious shortcomings inherent in the official method for determining pentosans, the present work was undertaken.

Historical

Formation of Furfural—Döbereiner (1832) first obtained furfural by the distillation of sugar with pyrolusite and sulfuric acid. Stenhouse (1840) later showed the pyrolusite to be unnecessary, while Völckel (1853) found that furfural was a decomposition product of many carbohydrate materials. Stenhouse (1850) was the first to prepare furfural on any appreciable scale. He distilled wheat bran with strong sulfuric acid. The use of a strong solution of zinc chloride in the distillation procedure was proposed by Babo (1853). Stone and Tollens (1888)

[1] Reprinted from *Ind. & Eng. Chem.*, **15**, 1167–1169 and 1255–1262, November and December, (1923).

and Wheeler and Tollens (1889) used sulfuric acid of various concentrations. Phosphoric acid was tried by Mann, Krüger, and Tollens (1896). Glacial acetic acid was used by Testoni (1917). It was early recognized, however, that the use of 12 per cent hydrochloric acid gave better yields of furfural, in a shorter time, with more accurate duplication of results, and with less "humin" formation, than when any other acid was used [Allen and Tollens (1890), Günther and Tollens (1890), de Chalmot and Tollens (1891), Councler (1892), Stone (1897), Hauers and Tollens (1903), Jolles (1905), Ling and Nanji (1921)]. Moreover, even acid of 12 per cent concentration has an appreciable destructive effect on furfural, a shown by Fraps (1901), Jolles (1905), Mayer and Tollens (1907), and van Haarst and Olivier (1914), and also upon pentose as argued by Unger and Jäger (1903), and Fraps (1915). Also, araban and fucosan, as well as the corresponding sugars, produce furfural very slowly so that the yield from them is lower than that from others of the group due to the destructive action of the acid, as has been shown by the above-mentioned writers and by Kunz (1916). The yields of furfural usually obtained are recorded in Table I

TABLE I—YIELDS OF FURFURAL OBTAINED FROM PENTOSE SUGARS BY DISTILLATION WITH ACIDS

Pentose Recovery Per cent	Yield of Furfural Per cent	OBSERVER
	Arabinose	
75.00	48.00	Browne (1912)
74.32	47.56	Unger and Jäger (1903)
74.54 to 82.35	47.7 to 52.7	DeChalmot and Tollens (1891)
73.44	47.00	MacKenzie (1913)
100	64.00	Ling and Nanji (1921)
98.7 to 100.8	64.00	Jolles (1905)
	Xylose	
89.85	57.50	Unger and Jäger (1903)
90.00	57.60	Browne (1912)
87.5 to 92.2	56 to 59	DeChalmot and Tollens (1891)
97.5 to 100.3	64.00	Jolles (1905)

Substances other than pentose may also yield furfural on distillation with acid. Glucuronic acid is one of these, and Tollens (1909) has determined it by a method identical with that for pentoses. However, glucuronic acid is rarely encountered. It has also been claimed that oxycellulose produces furfural. This statement appears to be based on the early work of Cross, Bevan, and Beadle (1894), Vignon (1899), and Faber and Tollens (1899), which was done before the production of hydroxymethylfurfural from hexose materials was established. Moreover, much of the furfural said to be produced from cellulose may really have its origin in true pentosans (hemi- and ortho-pentosans) contained in the cellulose. [König and Rump (1914), Schwalbe (1918), Heuser and Haug (1918), Schwalbe and Becker (1920).] Other interfering substances have been mentioned, but little is known concerning their composition and distribution. Bray and Staidl (1922) claim to have worked out a correction to lessen the error due to these substances, but have not published it.

TESTS FOR FURFURAL—For determining when distillation is complete, aniline acetate has usually been used. This is prepared by adding glacial acetic acid to a mixture of equal parts of colorless aniline and water until the mixture suddenly clears. It has been frequently observed, however, that acetic acid often gives a positive test, due to the presence in it of furfural, as was shown by V. Meyer (1878). To avoid the difficulty, the use of concentrated hydrochloric acid has been recommended by Tolman and Trescott (1906), Cunningham and Doree (1914), and Schorger (1917); but strong mineral acids may destroy the color, as has been argued by de Chalmot (1893) and by Baker and Hulton (1916). Hydroxymethylfurfural, arising from hexoses during acid distillation, does not interfere, since it is formed

so slowly and in such small quantities [van Ekenstein and Blanksma (1910), Cunningham and Doree (1914)]. Jolles (1905) believed the aniline test was not sufficiently sensitive, and used Bial's orcinol-ferric chloride test solution. Van Haarst and Olivier (1914) preferred phloroglucinol. The present official method for the determination of pentoses makes no mention of the use of an indicator. Distillation is simply carried out at a definite rate until a definite volume of distillate has been received.

Official Method and Suggested Modifications

The official method of distillation is to heat the sample with 12 per cent hydrochloric acid at such a rate that 30 cc. pass over in 10 minutes. Thirty cubic centimeters more of 12 per cent acid are then added and the process is repeated until 360 cc. of distillate have been collected.

The following modifications have been proposed:

Cross, Bevan, and Smith (1895) suggested the use of the constant level apparatus of Chorley (1895), and Stanek (1900) devised an automatic apparatus to facilitate the procedure, but these have not come into use. Heuser (1921) found that higher and more accurate yields of furfural were obtained if the weighed sample of pentosan was dissolved in normal sodium hydroxide solution before distilling with acid. Dekker (1914) added 500 cc. of 12 per cent hydrochloric acid and distilled directly. His results were low. Grund (1902) added and distilled in 50-cc. fractions and recorded a more intensive action by the change. Jolles (1905) added the acid, and steam-distilled the hydrolysate, heating the latter so that its volume decreased to about half while 800 cc. of water were distilled through it. More acid was then added and the process repeated until no more furfural was produced. Jolles claimed to get theoretical conversions of pentoses (arabinose and xylose) to furfural, the only such claim made in the literature.

Experimental

Materials—The following pentose materials were used:

l-Arabinose, $[\alpha]_D^{20} = 103.77°$
d-Xylose, $[\alpha]_D^{20} = 18.81°$

As pentosan-containing materials, pine sawdust and gum arabic were used, each being ground to 50 mesh. These materials were distilled with acid according to the procedures outlined below and the furfural-containing distillate was titrated by the method proposed in Part II, which is briefly as follows:

Method of Determining Furfural—A small aliquot of the distillate was titrated with standard alkali to determine its acidity. This aliquot was then re-added to the distillate and sufficient hydrochloric acid or strong sodium hydroxide solution also added to give a final acidity of about 4 per cent. Ten cubic centimeters of 20 per cent potassium bromide were then added and the resulting solution was titrated with standard potassium bromate solution in the manner described in Part II.

Indicator—For deciding when distillation was complete, strips of filter paper were used which had been dipped in aniline hydrochloride solution and dried. The aniline hydrochloride solution was freshly prepared from colorless aniline and C. P. hydrochloric acid.

Effect of Acidity during Distillation—Owing to the ease with which furfural is destroyed by strong acid, a study of the acidities obtained during distillation was regarded essential. Two 12 per cent hydrochloric acid distillation procedures were studied—(1) the method of the Association of Official Agricultural Chemists (1920), which has been said to yield low furfural figures; and (2) the method of Jolles, in which theoretical yields were claimed. In both studies the boiling point temperatures were taken as an index to the concentration of acid present in the distillation flasks.

Official Distillation Procedure—The samples were distilled as directed in the official method until 360 cc. had distilled over. In each instance the distillation began at 103° to 104° C., but had reached 108.55° C. (corrected) by the time 60 cc. had been distilled out. Subsequent additions of 12 per cent hydrochloric acid caused a temporary drop of 0.6° C., but the constant boiling temperature was very soon again reached. The greater part of the distillation took place, therefore, from acid of 18 to 20 per cent concentration. The data are recorded in Table II. The furfural in the distillate was determined by the titrimetric method described in Part II of this paper.

Table II—Pentose Determinations. Distillations by the Official Method

(Volume of distillate, 360 cc.)

Weight of Sample Gram	0.1 *N* $KBrO_3$ Cc.	Pentose Found (Factor = 0.007505) Gram		Recovery Per cent
		Arabinose		
0.2016	25.50	0.1914		94.9
0.2005	25.75	0.1943		96.8
0.2020	25.35	0.1903		94.2
0.2045	26.00	0.1951		95.4
			Average	95.3
		Xylose		
0.2038	26.00	0.1951		95.7
0.2022	25.75	0.1943		96.1
0.2016	25.80	0.1936		96.0
0.2009	25.75	0.1943		96.7
			Average	96.1

It will be noted that a recovery of 95.3 per cent from arabinose and 96.1 per cent from xylose was secured. These values are higher than have been found by most workers with the exception of Jolles (1905), and (possibly) Ling and Nanji (1921). Both Jolles and Ling and Naji, as well as the writers, used titrimetric methods for determining the furfural. If the higher results which the writers obtained are not due to a more accurate method of determining the furfural in the distillate, they are at a loss to explain their high values, especially those of arabinose.

Distillation Method of Jolles—Jolles advised that the pentose sample be placed in a distilling flask with 200 cc. of 12 per cent hydrochloric acid and steam-distilled, boosting at such a rate that the volume decreased to about 100 cc. while the steam from 800 cc. of water was led through it. More 12 per cent hydrochloric acid was then added, and the process repeated as long as furfural was produced. The

TABLE III—PENTOSE DETERMINATIONS. DISTILLATIONS BY STEAM FROM 12 AND 20 PER CENT HYDROCHLORIC ACID SOLUTIONS

Per cent Acid	Weight of Sample Gram	Volume of Distillate Cc.	0.1 *N* $KBrO_3$ Cc.	Pentose Found (Factor = 0.007505) Gram	Recovery Per cent
		Arabinose			
12	0.2030	715	27.00	0.2026	99.8
	0.2020	650	27.00	0.2026	100.3
	0.2014	900	26.80	0.2011	99.9
	0.2005	1200	26.70	0.2004	99.9
20	0.2030	1250	26.75	0.2008	100.2
	0.2040	755	26.75	0.2008	100.2
	0.2000	900	26.75	0.2008	100.3
	0.2010	1050	26.75	0.2008	99.9
				AVERAGE	100.1
		Xylose			
12	0.2003	400	26.65	0.2000	99.8
	0.2010	620	26.75	0.2008	99.9
	0.2040	1000	27.00	0.2026	99.3
	0.2020	425	26.85	0.2015	99.7
20	0.2035	300	27.25	0.2045	100.4
	0.2045	375	27.25	0.2045	100.0
	0.2033	500	27.15	0.2038	100.2
	0.2016	825	26.80	0.2011	99.8
				AVERAGE	99.9

temperatures obtained during this type of distillation were always from 103° to 104° C., which indicated that the acidity of the hydrolysate remained in the neighborhood of 12 per cent throughout the distillation. The lack of destruction of furfural observed by Jolles must then be due either to the low acidity during distillation, or to the prompt removal of the furfural by the current of steam passing through, or both.

To determine which of these factors was the more important, samples of pure pentoses and of the pentosan materials mentioned above were distilled with steam from both 12 and 20 per cent hydrochloric acid. The heat was adjusted so that temperatures of 103° to 104° C. were maintained in the 12 per cent distillation, while temperatures of 107° to 108° C. were held in the 20 per cent distillations. Within the limits of experimental error, theoretical results were in all cases obtained from the pentoses used, regardless of the concentration of acid. This is shown in Table III. The pentosan materials gave constant yields, indicating that no loss of furfural had occurred. (Table IV) Furthermore, the rate of distillation did not affect the yield, as shown by the marked differences in volumes of distillates obtained. Evidently, even a slow current of steam is sufficient to sweep out the furfural as fast as it is formed from the pentoses.

A comparison of the pentose results in Tables II and III indicates that the reason low results are obtained by the official method is that some of the furfural is destroyed by long contact with strong acid. Moreover, this destructive effect can be entirely eliminated by carrying a slow current of steam through the hydrolysate, thereby removing the furfural as fast as it is produced. Hence the following method for the quantitative production of furfural from pentose materials is proposed.

PROPOSED METHOD FOR DISTILLATION OF PENTOSES—Place a weighed (0.20 to 5.0 grams depending upon the pen-

TABLE IV—PENTOSAN DETERMINATIONS. DISTILLATIONS BY STEAM FROM 12 AND 20 PER CENT HCl SOLUTIONS

Per cent Acid	Weight of Sample Grams	Volume of Distillate Cc.	0.1 *N* $KBrO_3$ Cc.	Pentosan Found (Factor = 0.006605) Gram	Pentosan Per cent
		Gum Arabic			
12	0.5018	820	24.50	0.1618	32.2
	0.5033	1160	24.25	0.1602	31.8
	0.5053	725	24.65	0.1628	32.2
	0.5016	925	24.40	0.1611	32.1
20	0.5004	640	24.25	0.1602	32.0
	0.5053	685	24.50	0.1618	32.0
	0.5047	940	24.50	0.1618	32.1
	0.5036	900	24.50	0.1618	32.1
				AVERAGE	32.1
		Sawdust			
12	1.0020	935	23.25	0.1535	15.3
	1.0017	875	23.25	0.1535	15.3
	1.0056	1000	23.35	0.1542	15.3
	1.0064	900	23.50	0.1552	15.4
20	2.0020	615	46.40	0.3064	15.3
	2.0014	710	46.25	0.3054	15.3
	2.0049	625	46.50	0.3071	15.3
	2.0032	600	46.50	0.3071	15.3[a]
12	1.0026	575	23.00	0.1519	15.1[a]
	1.0077	870	23.25	0.1535	15.2[a]
	1.0018	530	23.25	0.1535	15.3[a]
				AVERAGE	15.3

a These distillations were carried out according to Heuser's method (1921), the samples being macerated with 4 per cent sodium hydroxide before distilled with acid. No increased yield of pentosan was obtained. Heuser's determinations always ran 4 per cent higher by this treatment. Hence the foregoing data further substantiate the claim that theoretical yields of furfural are obtained from pentosans by the proposed distillation procedure.

tose or pentosan content) sample of the material, and 200 cc. of 12 per cent hydrochloric acid (specific gravity, 1.06) in a 750-cc. distilling flask fitted up for steam distillation. Conduct a slow current of steam into the mixture and as soon as the mixture reaches the boiling temperature heat the distilling flask with a low flame so that the boiling temperature remains between 103° to 105° C. as measured by a thermometer inserted in the vapor in the neck of the distilling flask. By observing this precaution the addition of fresh

TABLE V—PENTOSE DISTILLATIONS BY THE PROPOSED METHOD

Weight of Sample Gram	0.1 *N* $KBrO_3$ Cc.	Factor = $\frac{\text{Grams Pentose}}{\text{Cc. 0.1 } N \text{ } KBrO_3}$
	Arabinose	
0.2000	26.50	0.00755
0.2005	26.50	0.00755
0.2015	26.75	0.00753
0.2021	26.85	0.00752
0.2030	27.00	0.00752
0.2025	27.00	0.00750
0.2037	27.25	0.00747
0.2040	27.25	0.00748
	AVERAGE	0.007515
	Xylose	
0.3020	40.00	0.00755
0.3035	40.30	0.00753
0.3010	40.00	0.00752
0.3027	40.30	0.00751
0.3040	40.45	0.00754
0.3070	41.00	0.00749
0.3082	41.20	0.00749
0.3044	40.50	0.00752
	AVERAGE	0.007519
	TOTAL AVERAGE	0.007517
	THEORETICAL	0.007505

acid will rarely be required. About one-half of the original volume of liquid should remain in the flask at the end of the distillation. Continue distillation until a drop of the distillate no longer gives a red coloration with aniline test paper on being allowed to stand 3 to 5 minutes.

By following this procedure theoretical yields of furfural have been obtained from all the pure pentose materials which have been tested. Representative data are found in Table V.

Conclusions

The data presented seem to warrant the following conclusions:

1—Distillations of pentose materials, carried out according to the method of the Association of Official Agricultural Chemists, take place from hydrochloric acid of 18 to 20 per cent concentration, instead of from 12 per cent acid as usually stated.

2—Hydrochloric acid of this concentration has a considerable destructive effect on furfural, and is no doubt partly responsible for the low yields of furfural that are obtained from all pentoses when the official method is used.

3—The passage of a slow current of steam through the distillation mixture is sufficient to carry the furfural off as rapidly as it is formed, thereby avoiding the destruction of furfural by long contact with strong acid.

II—The Determination of Furfural

Several new volumetric methods for the determination of furfural in dilute aqueous solution were tested out. Iodine in alkaline solution could not be used because the results could not be accurately duplicated. The trials with acid permanganate were also unsuccessful, owing to catalytic reduction of the permanganate by furfural. The use of potassium bromate in acidified furfural solutions containing potassium bromide was eminently successful.

Specific directions are given for obtaining theoretical yields of furfural from pentose materials and for the volumetric determination of this substance in the resulting distillates. Representative results of determinations on pure pentoses and pure furfural are recorded which seem to justify the use of the following theoretical factors for the conversion of potassium bromate used to furfural, pentose, pentosan, or the corresponding methyl derivatives:

Factors for Converting Grams of $KBrO_3$ Used

	Method of Calculation	Factor	Log
Furfural	$3C_5H_4O_2 : KBrO_3$	1.7254	0.236890
Pentose	$3C_5H_{10}O_5 : KBrO_3$	2.6961	0.430736
Pentosan	$3C_5H_8O_4 : KBrO_3$	2.3726	0.375225
Methylfurfural	$3C_6H_6O_2 : KBrO_3$	1.9758	0.295743
Methylpentose	$3C_6H_{12}O_5 : KBrO_3$	2.9481	0.469542
Methylpentosan	$3C_6H_{10}O_4 : KBrO_3$	2.6244	0.419024
Rhamnose hydrate	$3C_6H_{12}O_5H_2O : KBrO_3$	3.2717	0.514782

FACTORS FOR CONVERTING CUBIC CENTIMETERS OF 0.1 *N* $KBrO_3$ USED

Furfural	0.0027837 × Factor	0.004803	$\bar{3}.681513$
Pentose	0.0027837 × Factor	0.007505	$\bar{3}.875351$
Pentosan	0.0027837 × Factor	0.006605	$\bar{3}.819873$
Methylfurfural	0.0027837 × Factor	0.005500	$\bar{3}.740363$
Methylpentose	0.0027837 × Factor	0.008207	$\bar{3}.914184$
Methylpentosan	0.0027837 × Factor	0.007305	$\bar{3}.863620$
Rhamnose hydrate	0.0027837 × Factor	0.009107	$\bar{3}.959375$

MANY reagents have been proposed for the estimation of the furfural obtained from the acid distillation of pentose. The principal ones are reviewed below.

AMMONIA—The earliest method proposed was that of Stone and Tollens (1888),[1] which involved the precipitation of the furfural by ammonia and subsequent weighing of the resulting furfuramide. The method was quite unsatisfactory owing to incomplete precipitation of the furfural [Günther, de Chalmot and Tollens (1891), Stone (1891)].

PHENYLHYDRAZINE—This was proposed by the work of Fischer (1884). Günther and Tollens (1890) and Günther, de Chalmot, and Tollens (1891) titrated furfural with a standardized phenylhydrazine solution using aniline acetate paper as indicator. Stone (1891) used Fehling's solution to determine the end point. Ling and Nanji (1921) precipitated the furfural and determined the excess phenylhydrazine by iodometry. Flint and Tollens (1892) and others have shown that the use of this reagent in volumetric estimations is rather unsatisfactory owing to instability of the solution and the fact that it reacts with levulinic acid arising from hexoses, giving an indefinite end point. Phenylhydrazine was also used as a gravimetric reagent [de Chalmot and Tollens (1891), de Chalmot (1893, 1894)], Günther, de Chalmot, and Tollens (1891), Flint and Tollens. (1892), and Mann, Krüger, and Tollens (1896) undertook comparative studies of all the phenylhydrazine methods, and concluded that the gravimetric method was best. However, the furfural hydrazone was difficult to dry properly and conversion factors had to be determined experimentally. This reagent has also been used in the gaseometric determination of furfural [Gregore and Carpiaux (1898), Menaul and Dowell (1919)].

PYROGALLOL—Hotter (1893) heated acidified furfural solutions with pyrogallol in sealed tubes at 110° C. and weighed the resulting precipitates.

SEMIOXAMIZINE—This was used by Kerp and Unger (1897), who obtained low results with its use. Kreeman and Klein (1917) also used it in their study of the kinetics of the reaction whereby pentoses are transformed into furfural.

PHLOROGLUCINOL—Wheeler and Tollens (1889) first applied phloroglucinol as a color test, and Councler (1894) adapted the test to the gravimetric estimation of furfural. The method was studied by Welbel and Zeisel (1895), Mann, Krüger, and Tollens (1896), Tollens (1902), and Grund (1902). The first of these found that methylfurfural was also precipitated so that methylpentoses could be determined by the same method [Votocek (1897), Widtsoe, and Tollens (1900)]. Kröber (1900, 1901) amplified and perfected the whole pentose procedure and determined by actual experiment the factors and tables for the conversion of various weights of phloroglucinol precipitate into the corresponding weights of arabinose, xylose, pentose, and pentosan. Kröber's results were verified by Kröber, Rimbach, and Tollens (1902, 1902*a*). Mayer and Tollens (1907) then extended the Kröber procedure to include fucose, while Ellett and Tollens (1905) did the same for rhamnose. The latter investigators further found that both methylpentoses and pentoses

[1] For references see bibliography at end of article.

could be estimated in the same sample by applying Votocek's (1897) observation on the relative solubilities of methylfurfural and furfuralphloroglucide in 95 per cent alcohol at 60° C. Ishida and Tollens (1911) advised the use of a Soxhlet apparatus in the alcoholic extraction, but Schorger (1917) showed that this is less accurate than simple maceration of the precipitate with alcohol. Schorger further claimed that the procedure of Ellett and Tollens gave results which were too high for both pentose and methylpentose. Pinoff (1905) studied the reaction between furfural and phloroglucinol in alcoholic solution. Böddinger and Tollens (1910) proposed shortening the time required for precipitation by heating the solution, but this modification has been criticized [Wichter and Tollens (1911), Schorger (1917)]. Welbel and Zeisel (1895) advised weighing the precipitate in a weighing bottle because they believed it to be oxidized during drying and weighing in air. This contention was supported by Goodwin and Tollens (1904) and by Cunningham and Doree (1914), but denied by Mann, Krüger, and Tollens (1896), and Kröber (1900). Kröber (1901) found that on exposure to the air the precipitate took up moisture which was later removed with difficulty.

This conflicting evidence prompts the suspicion that the furfuralphloroglucinol precipitate does not have a fixed chemical composition. Various molecular proportions between furfural and phloroglucinol are cited by different writers, who further disagree as to the number of water molecules that are eliminated in the reaction. Goodwin and Tollens (1904) claimed that one molecule of water split out at ordinary temperature while at 80° C. three were lost. Kröber, in compiling his tables and formulas, assumed that two molecules were eliminated. Evidently, no two have had the same pure compound for analysis. The latest work is that of Votocek and Potmesil (1916) in which furfural was used to precipitate phloroglucinol from acid solution. These experimenters found, from a large number of determinations, that the ratio of condensation product to phloroglucinol was "about 2 : 1." Goodwin and Tollens and Kröber stated, however, that the variable composition of the precipitate could probably be disregarded without introducing any appreciable error. This is due to the purely empirical nature of the method.

Barbituric Acid Derivatives—The use of barbituric acid was suggested by Conrad and Reinbach (1901), and developed by Jäger and Unger (1902, 1903). Fromherz (1907), and Dox and Plaisance (1916) criticized the method, and the latter investigators also found malonylguanidine to be unsatisfactory. They found, however, that thiobarbituric acid precipitated furfural quantitatively from acid solution as a definite, crystalline chemical compound. They also suggested that the proportions of methylfurfural and furfural present could be calculated from the nitrogen and sulfur content of the precipitate. Hydroxymethylfurfural did not interfere.

Sodium Bisulfite—Jolles (1905) proposed the addition of an excess of standard sodium bisulfite solution to a neutralized aliquot of the distillate and titration of the excess by iodine. He also estimated both pentoses and methylpentoses by precipitating the former as barium pentosate [Bey (1900)] and performing a double distillation [Jolles (1907)]. The method was studied by Tolman and Trescott (1906) and Kerp and Wöhler (1909), who found that conditions had to be closely duplicated to obtain concordant results.

Fehling's Solution—The reduction of Fehling's solution by furfural was proposed as a possible method by Flohil (1911) and further studied by Eynon and Lane (1912) and by Baker and Hulton (1916), who found the presence of sodium chloride to be an influencing factor.

Silver Oxide—The oxidation of furfural by ammoniacal

silver oxide was used in a volumetric procedure by Cormack (1900), who titrated the excess silver by thiocyanate after filtration of the silver precipitate. Cormack's method has never been applied to the determination of pentoses.

Present Official Method

The method of the Association of Official Agricultural Chemists (1920) is essentially the Kröber modification of the Tollens method. To the distillate obtained, as previously described, an amount of phloroglucinol double that of the furfural expected is then added and the volume made up to 400 cc. with 12 per cent hydrochloric acid and allowed to stand over night. The amorphous precipitate is filtered off, washed, dried, and weighed in a tared Gooch crucible. After applying a solubility correction, the corresponding weight of pentose or pentosan is calculated using Kröber's factors.

The principal points of criticism of the present method are:

1—The method is empirical and is not based on the molecular weight of the condensation product; moreover, solubility corrections are necessary [Dox and Plaisance (1916)].

2—Theoretical yields of furfural are rarely, if ever, obtained.

3—The actual yields of furfural are conditioned by the rate of distillation and by the concentration of acid [de Chalmot (1893, 1894), Councler (1894), Welbel and Zeisel (1895), Wenzel and Lazar (1913), Falada, Stein and Ravniker (1914), van Haarst and Olivier (1914), Kreeman and Klein (1917)]. The usual yields of furfural obtained are recorded in Table I.

4—The various pentoses all yield different amounts of furfural. Kröber, therefore, as well as Tollens (1896), had to use a different factor in his calculations for each specific sugar. Hence an unknown material should be examined qualitatively. All the recorded data on the pentosans in wood are unreliable, since woods usually contain both araban and xylan [Schorger (1917), Schwalbe (1919)]. The presence of certain substances in the sample may prevent the liberation of the furfural [Seilliere (1909)].

5—Phloroglucinol precipitates substances other than furfural which are frequently present. Hydroxymethylfurfural, produced from hexose materials, is the chief one of these. [Düll (1895), Kiermayer (1895), Müther and Tollens (1904), van Ekenstein and Blanksma (1910), Jäger and Unger (1902), Kröber, Rimbach and Tollens (1902)]. The interference of this substance has been avoided by fermentation of the hexoses [Spoehr (1919)] and by redistilling the distillates [Fraps (1901), Cunningham and Doree (1914), Oshima and Konds (1918)]. The former method is inaccurate owing to fermentation of pentoses [Gillet (1917), Cross and Tollens (1912), Pellet (1916)], while in the latter method furfural is destroyed [Fraps (1901), van Haarst and Olivier (1914)]. Moreover, the fact that hydroxymethylfurfural phloroglucide is soluble in alcohol casts doubt on the existing methylpentosan data [Cunningham and Doree (1914)]. Schorger (1917) further points out that woods have never been proved to contain methylpentosans.

6—Substances other than pentose may yield furfural in the distillation. Glucuronic acid is the only compound for which this has been proved [Tollens (1909)], although oxycellulose, fats and oils, and their decomposition products are said to yield furfural [Bray and Staidl (1922)].

Experimental

Preliminary Tests

In the search for a satisfactory method for the determination of furfural, several procedures were tested out.

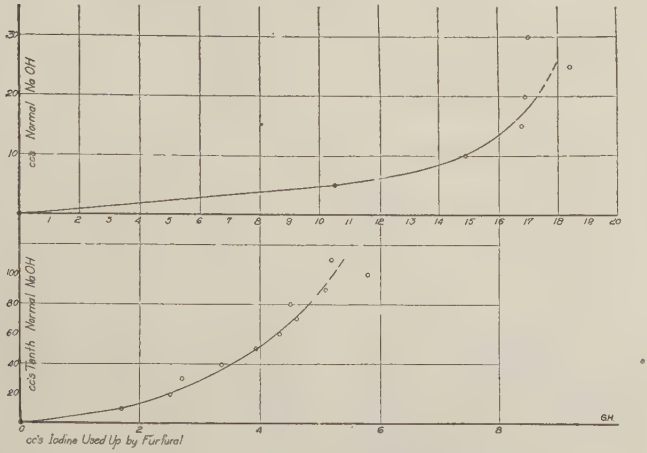

Fig. 1—Furfural Titrations with Hypoiodite

Sodium Hypoiodite—It was at first thought that iodine would be suitable. This reagent reacted with furfural only in alkaline solution. Moreover, the amount of iodine taken up was almost a direct function of the alkalinity, if the latter was low, as indicated in Fig. 1, while in strongly alkaline solutions concordant results could not be obtained. Although the amount of iodine used up appeared to approach a maximum, the results could not be accurately duplicated.

Acid Permanganate—Acid permanganate was then tried, but soon abandoned because large and indefinite volumes of permanganate were reduced to manganese dioxide by small quantities of furfural.

Potassium Bromate—At this point the use of potassium bromate was suggested by the work of Okuda (1919) on the oxidation of cystine. This reagent reacts as follows in acidified potassium bromide solution [Treadwell and Hall (1919)]:

$$KBrO_3 + 5KBr + 6HCl = 3Br_2 + 6KCl + 3H_2O$$

According to Wedekind (1901) furfural can be readily oxidized and brominated in aqueous solution. It was therefore hoped that the reaction between furfural and bromine[2]

[2] After the work of the writers was completed, attention was called to the work of Van Eck ["Versl. v. d. Verricht. v. h. Centr. lab. v. d. Volksgezondh.," **1918**; *C. A.*, **14**, 509 (1920)], who attempted to determine furfural by adding an excess of 0.1 *N* bromine in potassium bromide and determining the excess bromine over that reacting with the furfural. Details of his method are not available. The writers have been unable to secure satisfactory results by any method which involves adding an excess of bromine.

could be made the basis of a satisfactory method for the determination of furfural, provided an accurate means of finding the end point could be devised. Okuda used the yellow color due to free bromine as indicating the end point. In a preliminary test it was found that this could more accurately be found by the use of a simplified electrometric apparatus. With the use of the latter, a study of the optimum conditions for the titration of furfural by potassium bromate in acidified potassium bromide solution was undertaken.

Materials

Two specimens of furfural were used, one of which was obtained from a supply house, while the other had been prepared by graduate students working in the department of chemical engineering. Both samples distilled at 159° to 160° C., giving pale straw-colored distillates. Under reduced pressure these gave water-white distillates, which were used in making up the furfural solutions. All the solutions titrated had been freshly prepared from colorless furfural only a few hours previously. Old furfural solutions usually gave results which were somewhat in excess of the theory. A weighed quantity of the furfural was dissolved in distilled water and made up to a definite volume, from which aliquots were withdrawn for analysis.

"Chemically pure" potassium bromate was used, which, after drying, gave on analysis 99.99 per cent $KBrO_3$. The 0.1 *N* solution requires 2.7837 grams per liter. The bromate solution was standardized according to the method recommended by Merck (1914), in which 30 to 40 cc. are added to an acidified potassium iodide solution and the mixture is allowed to stand several minutes, after which it is diluted and the iodine titrated with standard thiosulfate in the usual manner.

A 20 per cent solution of potassium bromide free from bromate was used.

Apparatus

The apparatus used consists of a galvanometer, a tapping key, and two platinum wires, one of which is sealed into the side of a small pipet and held at a fixed potential by immersion in an acidified solution of 20 per cent potassium bromide containing a trace of free bromine. The other platinum wire is immersed in the solution to be titrated in a beaker. The potential of this wire depends upon the composition of the solution being titrated. A small electric stirrer insures thorough mixing of the unknown solution.

Before beginning the titration, depression of the tapping key will cause the galvanometer to deflect several divisions to the right or left, depending upon the exact manner in which the connections are made, whereas after the titration is completed, the presence of an excess of bromine in the beaker will cause a throw of the needle in the opposite direction.

Obviously, when depression of the key causes no deflection, the potential of both platinum wires is the same and the concentration of free bromine in the solution being titrated is

TABLE VI—EFFECT OF ACIDITY ON THE TITRATION OF FURFURAL SOLUTIONS
(0.1002 gram of furfural used in each case)

HCl Per cent	0.1 *N* $KBrO_3$ Cc.	Furfural Found (Factor = 0.004803) Gram	Recovery Per cent
1.4	20.70	0.0994	99.2
1.4	20.75	0.0997	99.5
1.4	20.85	0.1001	100.0
1.5	20.70	0.0994	99.2
2.6	20.80	0.0999	99.7
2.6	20.88	0.1003	100.1
2.7	20.85	0.1001	100.0
2.8	20.83	0.1000	99.9
4.0	20.55	0.0987	98.5
4.1	21.00	0.1009	100.7
4.2	20.80	0.0999	99.7
4.3	20.95	0.1006	100.4
5.0	21.00	0.1009	100.7
5.2	22.60	0.1085	108.4
5.2	22.25	0.1069	106.7
5.3	22.15	0.1064	106.2
6.8	24.52	0.1178	117.6
7.0	25.00	0.1201	119.8
7.0	25.40	0.1220	121.8
7.2	24.80	0.1191	118.9

practically equal to that in contact with the other platinum wire in the pipet. This is the end point.

METHOD

In the preliminary experiments the titrations were carried out as follows: The bromate solution was added to the furfural solution rather slowly until near the end point, when three to five drops were added at a time until the point was found at which, at the end of 2 minutes, a mere trace of free bromine was present as indicated by no deflection of the needle on closing the galvanometer circuit. This was taken as the end point. Since the molecular ratio of furfural to potassium bromate was unknown, equal quantities of furfural were always used so that the buret readings would serve as an index to the accuracy of the work. The factor for converting the standard bromate solution into furfural was computed later (Table XI). It was used in this place to facilitate comparisons.

FACTORS AFFECTING THE TITRATION

ACIDITY OF THE SOLUTION—To 10-cc. volumes of a furfural solution 10 cc. of 20 per cent potassium bromide were added and the resulting solution diluted to about 100 cc. Varying amounts of hydrochloric acid were then added and the furfural was titrated with potassium bromate as already described. After titration of the furfural, 10 cc. of the solution were withdrawn and the acidity was determined by titration with standard alkali. The results are shown in Table VI. It is evident that the degree of oxidation of the furfural is a function of the acidity of the solution, but at low acidities (1.4 to 4.3 per cent hydrochloric acid) the process stops at the first stage and the further action of bromine takes place

only slowly. A more accurate study of this last point is discussed later. In the most weakly acid solutions the reaction appeared to occur rather slowly, so that the bromate could only be added drop by drop. When the acidity was 3 to 4 per cent, however, the bromine was liberated promptly and therefore much less time was required for the titration. Moreover, accurate results were easily obtained provided the acidity did not exceed 4 per cent. This acidity was therefore adopted as standard.

Specific Acid Used—The substitution of 4 per cent sulfuric acid by weight for hydrochloric acid had no influence on the results, as is shown in Table VII.

Concentration of Potassium Bromide—The second factor studied was the influence of the concentration of potassium bromide on the results. Solutions containing 0.1002 gram of furfural, 10 cc. of 20 per cent potassium bromide, and 3 to 4 per cent hydrochloric acid in total volumes varying from 100 to 1000 cc. were titrated with bro-

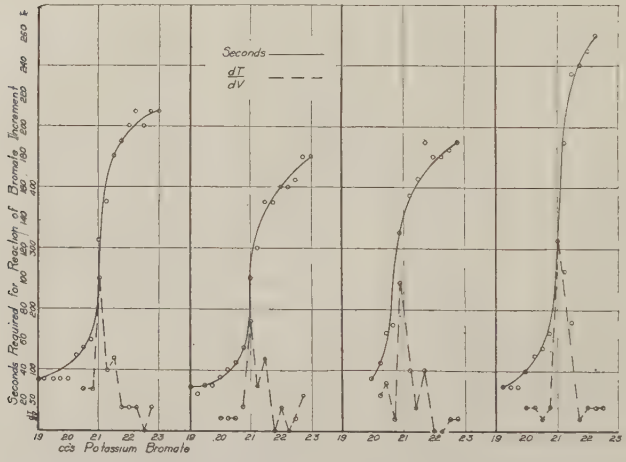

Fig. 2—Titration of Furfural with Bromine ($KBrO_3$ + HCl)

Table VII—Effect of Specific Acid Used
(0.1006 gram furfural used in each case)

Per cent by Weight	0.1 *N* $KBrO_3$ Cc.	Furfural Found (Factor = 0.004803) Gram	Recovery Per cent
	Hydrochloric Acid		
3.8	21.00	0.1009	100.3
4.0	20.75	0.0997	99.1
4.1	21.00	0.1009	100.3
	Average	0.1005	99.9
	Sulfuric Acid		
5.0	20.85	0.1001	99.5
4.2	20.85	0.1001	99.5
4.5	20.90	0.1004	100.2
4.0	20.75	0.0997	99.1
3.5	20.90	0.1004	100.2
6.0	21.00	0.1009	100.3
4.1	21.00	0.1009	100.3
4.2	20.80	0.0999	99.2
	Average	0.1003	99.8

mate. The results appear in Table VIII. It is apparent that the concentration of potassium bromide does not con-

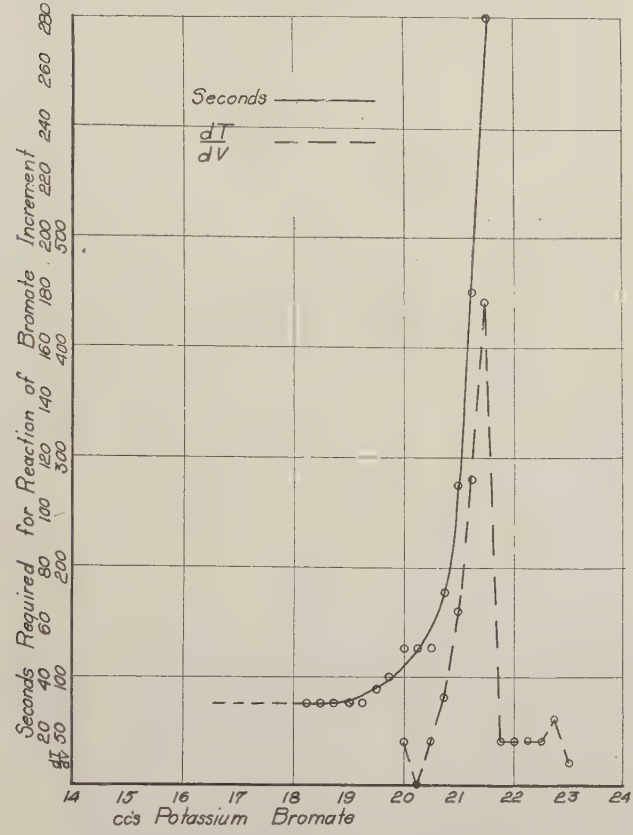

FIG. 3—ILLUSTRATION OF TYPICAL EXPERIMENT SHOWING HOW THE END POINT OF THE TITRATION IS OBTAINED

0.1 *N* $KBrO_3$	Time Sec.	dT Sec.	dV Cc.	$\frac{dT}{dV}$
18.30	30	..	0.25	...
18.55	30	0	0.25	0
18.80	30	0	0.25	0
19.05	30	0	0.25	0
19.30	30	0	0.25	0
19.55	35	5	0.25	20
19.75	40	5	0.25	20
20.00	50	10	0.25	40
20.25	50	0	0.25	0
20.50	50	0	0.25	40
20.75	70	20	0.25	80
21.00	110	40	0.25	160
21.25	180	70	0.25	280
21.50	290	110	0.25	440
21.75	300	10	0.25	40
22.00	310	10	0.25	40
22.25	320	10	0.25	40
22.50	330	10	0.25	40
22.75	345	15	0.25	60
23.00	350	5	0.25	20

0.1 *N* $KBrO_3$ required 21.50 cc.
Furfural found 0.1033 gram
Recovery 100.3 per cent

TABLE VIII—EFFECT OF CONCENTRATION OF POTASSIUM BROMIDE

(0.1002 gram furfural used in each case)

KBr Per cent	0.1 *N* $KBrO_3$ Cc.	Furfural Found Gram	Recovery Per cent
2.0	20.80	0.0990	99.7
1.0	20.75	0.0997	99.5
0.7	20.70	0.0994	99.2
0.5	20.90	0.1004	100.2
0.4	21.10	0.1013	101.2
0.4	21.40	0.1028	102.6
0.3	20.90	0.1004	100.2
0.3	22.00	0.1057	105.5
0.2	21.05	0.1011	100.9
0.2	21.35	0.1025	102.4
	AVERAGE	0.1012	101.1

sistently affect the titration. The irregular results are due to the fact that at the time these determinations were made the end point had not been carefully studied. A concentration of 1 per cent potassium bromide was used in all subsequent determinations.

CONCENTRATION OF FURFURAL—In Table IX are brought together the results of trials in which the concentration of furfural was varied while that of both hydrochloric acid and potassium bromide was maintained constant. It was concluded from these results that, within the limits studied, the concentration does not affect the accuracy of the titration.

RATE OF ADDITION OF BROMATE—In Table X are recorded some results in which the bromate solution was added rapidly until the end point was nearly reached. After all the bromine had disappeared the titrations were finished in the usual way. However, the results ran too high, showing that it was necessary to add the reagent slowly, avoiding the presence of any large excess of free bromine if accurate results

TABLE IX—EFFECT OF CONCENTRATION OF FURFURAL

(0.1002 gram furfural used in each case)

Furfural Per cent	0.1 *N* $KBrO_3$ Cc.	Furfural Found (Factor 0.004803) Gram	Recovery Per cent
0.10	21.10	0.1013	101.2
0.06	20.60	0.0989	98.8
0.05	20.90	0.1004	100.2
0.03	21.10	0.1013	101.2
0.02	21.05	0.1011	100.9
0.01	21.10	0.1013	101.2
0.01	20.95	0.1006	100.4
0.005	21.15	0.1016	101.4
	AVERAGE	0.1008	100.7

TABLE X—EFFECT OF RATE OF ADDITION OF BROMATE SOLUTION

(0.1002 gram furfural used in each case)

0.1 *N* $KBrO_3$			
Added Rapidly at Start Cc.	Final Titer Cc.	Furfural Found (Factor = 0.004803) Gram	Recovery Per cent
18.00	21.20	0.1018	101.6
19.00	21.45	0.1030	102.8
20.50	21.75	0.1045	104.3
	AVERAGE	0.1031	102.9
Added Slowly from Start Cc.			
20.70		0.0994	99.2
20.75		0.0997	99.5
21.00		0.1009	100.6
	AVERAGE	0.1000	99.8

were to be expected. In all subsequent work, therefore, the bromate was added slowly enough so that the solutions were never more than faintly yellow colored.

The End Point—Having established the proper acidity and concentration of bromide required for the titration, the next problem was to improve the technic so that more concordant results might be obtained.

Towards the end of the reaction between furfural and bromine the oxidation is quite slow so that the oxidation potential of the solution is never constant. Therefore, the potentiometric method of determining the end point was not found suitable. It was then decided to determine the end point by using the time factor itself in connection with the titration apparatus already described.

For this purpose solutions of known furfural content were titrated to within 2 or 3 cc. of the end point, when the addition of the bromate solution was continued in 0.25-cc. increments. The time required for each increment to interact was observed by the use of the galvanometer and a watch. As soon as the deflection fell to zero the next increment of bromate was added and the process repeated until the end point had been crossed. The time required for disappearance of the bromine was then plotted against the total volume of potassium bromate that had been added. Several characteristic curves are shown in Fig. 2. The shape of these curves indicates that there are two possible reactions between furfural and bromine, but that one of these is far more rapid than the other in the presence of 4 per cent acid. This causes the curves to rise almost perpendicularly after the principal reaction has been completed.

The selection of the end point from such curves is rather difficult. If, however, the value dt/dv, where dv is the increment of bromate added and dt is the increase in time required for its disappearance over that required by the preceding increment, is plotted against the total volume of bromate used, a curve is obtained which passes through a maximum at the end point. This is best shown by the specific example given in Fig. 3. The lower set of curves in Fig. 2 shows the advantage of this method of plotting the results. Each upper and lower curve was plotted from the same data. Thus, the end point of the titration is obtained by measuring the time required for 0.25-cc. increments of bromate to react and plotting dt/dv against the total volume. The abscissa corresponding to the point of maximum inflection of the curve is the true end point.

The results of a series of determinations on known solutions of colorless furfural run according to the foregoing procedure are recorded in Table XI. Since this procedure appeared eminently satisfactory, the factor for converting bromate to furfural was calculated from the results.

A comparison of the results in Tables VI to X with those in

Table XI shows much greater concordance in the latter. This suggests that the cause of error when an arbitrary 2-minute end point was used was probably the effect of small variations in acidity of the solution. However, such variations apparently affect both the reactions between furfural and bromine to nearly the same extent, so that when the results are plotted the end point is still readily located.

To verify this statement a final set of experiments was carried out in which the acidities were varied. The results are shown in Table XII and plotted in Fig. 4. The intensifying effect of the acid is clearly apparent from the slope of

TABLE XI—ANALYSES OF FURFURAL BY THE PROPOSED METHOD

Furfural Used Gram	0.1 *N* $KBrO_3$ Cc.	Factor Gram Pentose per Cc. 0.1 *N* $KBrO_3$	Furfural Found (Factor = 0.004803) Grama	Recovery Per cent
0.1007	21.00a	0.00480	0.1009	100.1
0.1007	21.00a	0.00480	0.1009	100.1
0.1007	20.90a	0.00482	0.1004	99.7
0.1007	21.10a	0.00477	0.1013	100.6
0.1007	21.05	0.00478	0.1010	100.3
0.1007	20.85	0.00483	0.1001	99.4
0.1007	20.95	0.00481	0.1006	99.9
0.2014	42.00	0.00480	0.2017	100.1
0.2014	42.00	0.00480	0.2017	100.1
0.2014	41.95	0.00480	0.2014	100.0
0.2014	42.05	0.00479	0.2018	100.2
0.2014	42.05	0.00479	0.2018	100.2
0.1030	21.40	0.00481	0.1027	99.7
0.1030	21.50	0.00479	0.1032	100.2
0.1030	21.60	0.00477	0.1037	100.6
0.1030	21.50	0.00479	0.1032	100.2
0.1030	21.50	0.00479	0.1032	100.2
0.2060	43.25	0.00476	0.2076	100.8
0.2060	43.00	0.00479	0.2064	100.2
0.2060	43.25	0.00476	0.2076	100.8
0.2060	43.00	0.00479	0.2064	100.2
	AVERAGE	0.004792		100.2
	THEORETICAL	0.004803		100.0

a The curves for these results appear in Fig. 2.

the upper set of curves. Nevertheless, the end points were readily found by replotting the data in the manner advised above.

CONVERSION FACTOR FOR FURFURAL

The factors in Table XI were obtained by dividing the number of cubic centimeters of 0.1 *N* potassium bromate used by the corresponding weight of furfural. A close agreement is apparent, the average being 0.004792. Moreover, the theoretical ratio, based on a molecular ratio of potassium bromate to furfural of 1:3, is 0.004803, from which the experimental factor differs by less than 0.3 per cent.

TABLE XII—ANALYSES OF FURFURAL BY THE PROPOSED METHOD IN SOLUTIONS OF VARYING ACIDITIES
(0.1112 gram furfural used in each case)

HCl by Weight Per cent	0.1 *N* $KBrO_3$ Cc.	Furfural Found Gram	Recovery Per cent
1.8	23.15	0.1112	100.0
4.0	23.15	0.1112	100.0
5.0	23.00	0.1105	99.3
6.1	23.25	0.1117	100.4
	AVERAGE	0.1111	99.9

This is well within the limits of experimental error of the method so that the use of the theoretical factor for the purpose of calculation is justified. Theoretical factors were used throughout in the present studies, a procedure which is impossible in the present official method for determining furfural and pentoses.

Effect of Interfering Substances on the Proposed Method

Furfural distillates from pentose-containing materials always contain levulinic acid and hydroxymethyl-furfural when hexose materials are present. Therefore, a study of the possible effect of these substances was undertaken.

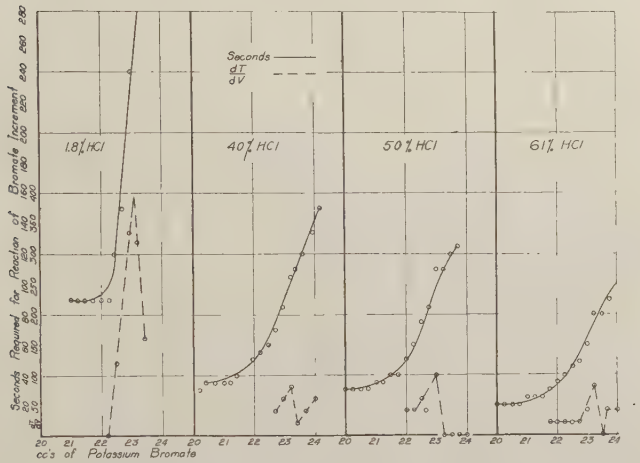

Fig. 4—Titration of Furfural with Bromate Solution in the Presence of Different Concentrations of Hydrochloric Acid

Levulinic Acid—Five determinations were run on furfural solutions containing varying amounts of Kahlbaum's levulinic acid. The results are recorded in Table XIII. It is evident that the presence of this substance had no influence on the results in the cases tried.

Table XIII—Effect of Levulinic Acid

(0.2016 gram furfural used in each case. Total volume before titration 100 cc.)

Levulinic Acid Added Grams	0.1 *N* $KBrO_3$ Cc.	Furfural Found (Factor = 0.004803) Gram	Recovery Per cent
0.3	41.90	0.2012	99.8
1.0	42.05	0.2020	100.2
2.0	42.00	0.2017	100.1
3.0	41.80	0.2008	99.6
5.0	42.00	0.2017	100.1
	Average	0.2015	100.0
0	42.00	0.2017	100.1
0	41.80	0.2008	99.6
0	42.15	0.2024	100.4
0	42.00	0.2017	100.1
	Average	0.2016	100.0

HYDROXYMETHYLFURFURAL—Since no supply of this substance was available, weighed samples of glucose, sucrose, lactose, and starch were distilled by the method adopted for pentoses and the distillates titrated. The results are shown in Table XIV. As a further check, the determinations shown

TABLE XIV—EFFECT OF HEXOSE CARBOHYDRATES
(2.0-gram samples used in each case)

Material Used	0.1 *N* $KBrO_3$ Cc.	Furfural Found (Factor = 0.004803) Gram	Furfural Per cent	Pentose Factor = 0.007505 Per cent
Glucose	1.00	0.0048	0.24	0.38
	0.50	0.0024	0.12	0.18
Sucrose	1.00	0.0048	0.24	0.38
	0.75	0.0036	0.18	0.28
Lactose	1.00	0.0048	0.24	0.38
	1.00	0.0048	0.24	0.38
Starch	0.75	0.0036	0.18	0.28
	0.75	0.0036	0.18	0.28
		AVERAGE	0.20	0.32

in Table XV were made, using mixtures of equal quantities of pentose and hexose. It is apparent from the results cited that hydroxymethyl furfural has a slight effect on the titration of furfural, but that this is small enough to be disregarded in many instances since the error thereby introduced is small. The probable explanation of the noninterference of hexoses seems to be that the hydroxymethyl furfural is converted, under the conditions of distillation, into levulinic acid, which is without effect.

TABLE XV—EFFECT OF HEXOSES ON DETERMINATION OF PENTOSES
(0.3 gram each of xylose and sucrose used in each case)

0.1 *N* $KBrO_3$ Cc.	Pentose Found (Factor = 0.007505) Gram	Recovery Per cent
39.90	0.2994	99.8
40.10	0.3010	100.3
40.10	0.3010	100.3
40.25	0.3021	100.7
40.35	0.3028	100.9
40.40	0.3032	101.1
40.50	0.3040	101.3
40.50	0.3040	101.3
	AVERAGE	100.7

METHYLFURFURAL—Inasmuch as methylfurfural might be expected to interfere, distillations of a methylpentose (rhamnose) were carried out. The rhamnose was prepared in this laboratory from quercitrin according to the method of Walton (1921) from the quercitrin in "lemon flavin." The rhamnose was analyzed and was found to be $C_6H_{12}O_5.H_2O$. The bromate titration values are shown in Table XVI. These indicate a recovery of 107 per cent using the same molecular ratio —i. e., $3C_6H_{12}O_5.H_2O : KBrO_3$—as was found for the pentose sugars. No explanation can be offered for this high value. There is no good evidence as to how widely methylpentosans are distributed in nature. These determinations indicate that if they are present they will form methylfurfural, which will be titrated in the proposed method and perhaps cause appreciable error in the pentosan values. Such an error,

TABLE XVI—EFFECT OF METHYL PENTOSE
(0.3-gram rhamnose hydrate used in each case)

0.1 N $HBrO_3$ cc.	Rhamnose Hydrate Found (Factor = 0.009107) gram	Recovery Per cent
35.29	0.3214	107.1
35.75	0.3256	108.5
35.54	0.3237	107.9
35.55	0.3238	107.9
35.50	0.3233	107.8
	AVERAGE	107.6

however, is present in all methods which have so far been proposed for pentosan derivatives, and it is believed that the bromate titration error will be much less than that incurred in the phloroglucinol method, owing to the other sources of error already present in that method.

From a study of these results the following method for the determination of furfural in aqueous solutions is suggested:

PROPOSED METHOD FOR DETERMINATION OF FURFURAL

To the solution containing 0.1 to 0.2 gram furfural, 5 cc. of 20 per cent potassium bromide are added for every 100 cc. of solution, and the acidity (HCl) is adjusted to about 4 per cent by weight by adding either acid or alkali as required. With continual stirring, 0.1 N potassium bromate solution is run in from a buret at such a rate that the production of a distinct yellow color throughout the solution is avoided. When the end point is approached a pale yellow color will be apparent immediately after the addition of a few drops of bromate solution, but this soon fades. When this point is reached the bromate is added in 0.2 to 0.3-cc. increments and the time is recorded which is required for the disappearance of free bromine, as indicated by the use of a galvanometer set-up as already explained. As the end point is crossed a rather large increase in the time required will be noted. The observations should be carried slightly beyond this point. Finally, the ratio of increment of time to increment of standard potassium bromate is plotted against the total value of potassium bromate already used, and the end point found from the curve thus obtained. The number of cubic centimeters of 0.1 N potassium bromate required multiplied by 0.004803 gives the grams of furfural in sample.

CONCLUSION

The studies concerning the potassium bromate method for the determination of furfural led to the following conclusions:

1—The acidity of the solution to be titrated should not exceed 4 or 5 per cent by weight, because

2—Further oxidation of the primary product of the interaction of bromine and furfural results in the presence of high concentrations of acid.

3—The velocity of this secondary reaction under the con-

ditions proposed appears to be so small as to be without appreciable effect on the titration.

4—Either hydrochloric or sulfuric acids may be used.

5—An approximate concentration of 1 per cent potassium bromide is satisfactory.

6—The potassium bromate solution must be added slowly, at all times avoiding the presence of any considerable excess.

7—The amount of furfural present does not influence the accuracy of the method.

8—In titrating dilute solutions with potassium bromate, the end point can be readily located by the use of a simplified electrometric apparatus consisting of two platinum wires, a galvanometer, and key.

9—The time factor of the reaction involved is made the basis of the foregoing method for finding the end point.

10—Hydroxymethylfurfural, a product of the acid distillation of hexose materials, apparently interferes slightly with the use of the proposed method. However, the effect is small enough to be disregarded.

11—Levulinic acid, a further decomposition product of hexoses, is without any effect whatsoever.

12—Methylpentoses or pentosans will interfere in that methylfurfural is formed which will titrate with the bromate solution.

Bibliography

Allen and Tollens, "Über Holzzucker (Xylose) und Holzgummi (Xylan)," *Ann.*, **260**, 289 (1890).

Association of Official Agricultural Chemists, Methods, **1920**, p. 96.

Babo, "Über die Darstellung des Furfurols," *Ann.*, **85**, 100 (1853).

Baker and Hulton, "The Estimation of Pentose or Pentosans by Means of Fehling's Solution," *Analyst*, **41**, 294 (1916).

Bey, "Zur physiologischen Chemie der Pentosen und Methylpentosan," *Z. klin. Med.*, **39**, 305 (1900); abstracted in *Chem. Zentr.*, **71**, I, 803 (1900).

Böddinger and Tollens, "Modification of the Furfural Method for the Estimation of Pentosans," *J. Landw.*, **58**, 232 (1910); abstracted in *Analyst*, **36**, 161 (1910).

Bray and Staidl, "The Chemical Changes Involved during Infection and Decay of Wood and Wood Pulp," *J. Ind. Eng. Chem.*, **14**, 35 (1922).

Browne, "Handbook of Sugar Analysis," **1912**, p. 449. John Wiley & Sons, Inc., New York.

Chorley, "Constant Level Apparatus," *Analyst*, **20**, 16 (1895).

Conrad and Reinbach, "Condensationen von Barbituresäure und Aldehyden," *Ber.*, **34**, 1339 (1901).

Cormack, "Estimation of Furfuraldehyde," *J. Chem. Soc.* (*London*), **77**, 990 (1900).

Councler, "Verzuckerung von Holzgummi mittelst Salzsäure," *Chem. Ztg.*, **16**, 1719 (1892).

Councler, "Ein neues Verfahren zur quantitativen Bestimmung von Furfurol, bezw. den in den Vegetabilien enthaltenen Pentosanen," *Chem. Ztg.*, **18**, 966 (1894).

Cross, Bevan, and Beadle, "Die naturlichen Oxycellulosen," *Ber.*, **27**, 1061 (1894).

Cross, Bevan, and Smith, "Über die Frage nach dem Ursprung ungesättigter Verbindungen in der Pflanze," *Ber.*, **28**, 1940 (1895).

Cross and Tollens, "Experiments on the Behavior of Pentoses in Fermenting Mixtures," *J. Landw.*, **59**, 419 (1912); abstracted in *C. A.*, **6**, 665 (1912).

Cunningham and Doree, "The Production of α-Hydroxy-s-methylfurfuraldehyde from Carbohydrates and Its Influence on the Estimation of Pentosans and Methylpentosans," *Biochem. J.*, **8,** 438 (1914).

De Chalmot, "Soluble Pentoses in Plants," *Am. Chem. J.*, **15,** 21 (1893).

De Chalmot, "Pentoses in Plants," *Am. Chem. J.*, **15,** 276 (1893); **16** 218 (1894).

De Chalmot and Tollens, "Über die quantitative Bestimmung von Pentaglycosen in Vegetabilien," *Ber.*, **24,** 694 (1891).

De Chalmot and Tollens, "Methode von de Chalmot und Tollens zur Furfurol- und Pentose-Bestimmung durch Destillation mit Salzsäure und gewichtsanalytische Bestimmung des Furfurols," *Ber.*, **24,** 3579 (1891).

Dekker (*See* Van Haarst and Olivier).

Döbereiner, "Über die medicinische und chemische Anwendung und die vortheilhafte Darstellung der Ameisensäure," *Ann.*, **3,** 141 (1831).

Dox and Plaisance, "A Comparison of Barbituric Acid, Thiobarbituric Acid, and Malonylguanidine as Quantitative Precipitants for Furfural," *J. Am. Chem. Soc.*, **38,** 2156 (1916).

Düll, "Über die Einwirkung von Oxalsäure auf Inulin," *Chem. Ztg.*, **19,** 216 (1895).

Ellett and Tollens, "Über die Bestimmung der Methylpentosane neben den Pentosanen," *Ber.*, **38,** 492 (1905).

Eynon and Lane, "The Estimation of Furfural by Means of Fehling's Solution," *Analyst*, **37,** 41 (1912).

Faber and Tollens, "Untersuchungen über die Oxycellulose," *Ber* , **32,** 2589 (1899).

Falada, Stein, and Ravniker, "Applicability of Tollens-Krüger Method for Determination of Pentosans," *Österr.-ung. Z. Zuckerind. Landw.*, **43,** 426 (1914); abstracted in *C. A.*, **8,** 3725 (1914).

Fischer, "Phenylhydrazin als Reagens auf Aldehyde und Ketone," *Ber.*, **17,** 572 (1884).

Flint and Tollens, "Über die Bestimmung von Pentosanen und Pentosen in Vegetabilien durch Destillation mit Salzsäure und gewichtsanalytische Bestimmung des entstandenen Furfurols," *Ber.*, **25,** 2912 (1892).

Flohil, "Estimation of Pentosans with the Aid of Fehling's Solution," *Chem. Weekblad.*, **7,** 1057 (1911); abstracted in *Analyst*, **36,** 161 (1911).

Fraps, "The Determination of Pentosans," *Am. Chem. J.*, **25,** 501 (1901).

Fraps, "Distribution and Digestibility of the Pentosans of Feeds," Texas Agr. Expt. Sta., *Bull.* **175,** 1 (1915).

Fromherz, "Zur quantitative Bestimmung des Methylfurols," *Z. physiol. Chem.*, **50,** 241 (1907).

Gillet, "Studies on the Quantity of Furfurosans or Substances Producing Furfural in the Different Products of the Beet Sugar Factory," *Bull. assoc. chim. sucr. dist.*, **35,** 93 (1917); abstracted in *C. A.*, **13,** 2296 (1917).

Goodwin and Tollens, "Über die Zusammemsetzung des Furfurolphloroglucide," *Ber.*, **37,** 315 (1904).

Gregoire and Carpiaux, "The Estimation of Pentoses," *Bull. de l'Assoc. Belge.*, **12,** 143 (1898); abstracted in *Analyst*, **24,** 39 (1899).

Grund, "Über den Gehalt des Organisms an gebundenen Pentosen," *Z. physiol. Chem.*, **35,** 111 (1902).

Günther and Tollens, "Über quantitative Bestimmung von Furfurol und Pentaglycosen," *Ber.*, **23,** 1751 (1890).

Günther, De Chalmot, and Tollens, "Über die Bestimmung des Furfurols und der in Vegetabilien enthaltenen Pentaglycosen und Pentosane," *Ber.*, **24,** 3575 (1891).

Hauers and Tollens, "Über die Hydrolyse Pentosan-haltender Stoffe mittels verdünnter Säuren und mittels Sulfitflüssigkeit, sowie über die Isolierung von Pentosen," *Ber.*, **36,** 3306 (1903).

Heuser, "Beitrage zur Kenntnis der Pentosane," *J. prakt. Chem.*, **103,** 69 (1921).

Heuser and Haug, "Über die Natur der Cellulose aus Getreidestroh," *Z. angew. Chem.*, **31,** 99, 168 (1918).

Hooker, "Pentosan Content in Relation to Winter Hardiness," *Proc. Am. Soc. Hort. Sci.*, **1920,** p. 204.

Hotter, "Eine neue Methode zur quantitativen Bestimmung der in den Vegetabilien vorkommenden Pentosanen," *Chem. Ztg.*, **17,** 1743 (1893).

Ishida and Tollens, "Über Bestimmung von Pentosan und Methylpentosan in Getriede und Holzpilzen. Die Trennung der Phloroglucide des Furfurols und des Methylfurfurols," *J. Landw.*, **59**, 61 (1911); abstracted in *Chem. Zentr.*, II, 794 (1911).

Jäger and Unger, "Über Pentosanbestimmung," *Ber.*, **35**, 4440 (1902).

Jolles, "Über ein neues Verfahren zur quantitativen Bestimmung der Pentosen," *Sitz. Akad. Wiss. Wien*, **114**, Abt. II, 1191 (1905).

Jolles, "Eine Methode zur quantitativen Bestimmung der Methylpentosen," *Ann.*, **351**, 38 (1907).

Kerp and Unger, "Über das Semioxamazid," *Ber.*, **30**, 585 (1897).

Kerp and Wohler, "The Sulfite-Cellulose Waste Liquor and Furfuraldehyde–Sulfuric Acid," *Arb. kais. Gesundh.*, **32**, 120 (1909); abstracted in *C. A.*, **4**, 443 (1909).

Kiermayer, "Über ein Furfurolderivat aus Lävulose," *Chem. Ztg.*, **19**, 1003 (1895).

König and Rump, "Chemistry and Structure of the Cell Membrane," *Z. Nahr. Genussm.*, **28**, 177 (1914); abstracted in *C. A.*, **9**, 815 (1914).

Kreeman and Klein, "Zur Kinetik der Furfurolbildung aus Pentosan (Arabinose)," *Monatsch.*, **38**, 63 (1917).

Kröber, "Pentosanbestimmungen mittels der Salzsäurephloroglucinmethode," *J. Landw.*, **48**, 357 (1900); abstracted in *Chem. Zentr.*, **72**, I, 477 (1901); *J. Landw.*, **49**, 7 (1901), abstracted in *Chem. Zentr.*, **72**, I, 1119 (1901).

Kröber, Rimbach, and Tollens, "Über die Bestimmung der Pentosen und Pentosane mittelst Salzsäure Destillation und Fällung des Furfurols durch Phloroglucin," *Z. angew. Chem.*, **15**, 477 (1902).

Kröber, Rimbach, and Tollens, "Anwendung der Pentosan-Bestimmungs-methode auf verschiedene vegetabilische Stoffe und die Materialien der Papierfabrikation," *Z. angew. Chem.*, **15**, 508 (1902).

Kunz, "Über Pentosane und die sogenannten Furfuroide," *Biochem. Z.*, **74**, 312 (1916).

Ling and Nanji, "A Method of Estimating Phenylhydrazine Volumetrically and Its Application to the Estimation of Pentosans and Pentoses," *Biochem. J.*, **15**, 466 (1921).

Mackenzie, "The Sugars and Their Simple Derivatives," **1913**, p. 147.

Mann, Krüger, and Tollens, "Über die Bestimmung der Pentosen und Pentosane durch Furfuroldestillation," *Z. angew. Chem.*, **9**, 33 (1896).

Mayer and Tollens, "Über die quantitative Bestimmung der Fucose und den Methylpentosane," *Ber.*, **40**, 2441 (1907).

Menaul and Dowell, "A Modification of the Phenylhydrazine Method of Determining Pentosans," *J. Ind. Eng. Chem.*, **11**, 1024 (1919).

Merck, "Chemical Reagents, Their Purity and Tests," **1914**, p. 127. Merck & Co., New York.

Meyer, "Notiz über das Vorkommen von Furfurol im käuflichen Eisessig," *Ber.*, **11**, 1870 (1878).

Müther and Tollens, "Über die Producte der Hydrolyse von Seetang (Fucus) Laminaria und Carraghen–Moos," *Ber.*, **37**, 298 (1904).

Okuda, "A Method for the Determination of Cystine," *J. Agr. Imp. Univ. Tokyo*, **7**, 69 (1919).

Oshima and Konds, "Detection of Methyl Pentosans," *J. Tokyo Chem. Soc.*, **39**, 185 (1918); abstracted in *C. A.*, **12**, 1276 (1918).

Pellet, "Sur la destruction totale des pentoses an cours de la fermentation alcoolique," *Compt. rend.*, **163**, 274 (1916).

Pinoff, "Studien über die Tollens'sche Phloroglucinsalzsäure Reaction auf Pentosen," *Ber.*, **38**, 766 (1905).

Rosa, "Pentosan Content in Relation to Hardiness in Vegetable Plants," *Proc. Am. Soc. Hort. Sci.*, **1920**, p. 207.

Schorger, "The Chemistry of Wood," *J. Ind. Eng. Chem.*, **9**, 556 (1917).

Schwalbe, "Scheme for the Analytical Investigation of Vegetable Fibrous Materials and the Cellulose Prepared from Them." *Z. angew. Chem.*, **31**, 193 (1918); abstracted in *C. A.*, **13**, 1016 (1919).

Schwalbe, "Ein Analysenschema für die chemische Untersuchung pflanzlicher Rohfasserstoff und daraus abgeschiedener Zellstoff," *Z. angew. Chem.*, **32**, I, 125 (1919).

Schwalbe and Becker, "Zur Reinigung von Zellstoffen," *J. prakt. Chem.*, **100**, 19 (1920).

Seilliere, "Sur une Cause Frequente d'Erreur dans le Dosage des Pentosanes," *Compt. rend. soc. biol.*, **66**, 310 (1909).

Spoehr, "Carbohydrate Economy of Cacti," *Carnegie Inst. Pub.*, **287**, 1 (1919).

Stanek, "Über einen antomatischen Apparat zur Bestimmung der Pentosane," *Z. Zuckerind. Böhmen*, **24**, 227 (1900); abstracted in *Chem. Zentr.*, **71**, I, 788 (1900).

Stenhouse, "Über das sogenannte künstliche Ameisenöl," *Ann.*, **35**, 301 (1840).

Stenhouse, "Über die Oele, die bei der Einwirkung der Schwefelsäure auf verschiedene Vegetabilien Enstehen," *Ann.*, **74**, 278 (1850).

Stone, "The Quantitative Determination of Furfurol and the Pentose Carbohydrates," *J. Anal. Appl. Chem.*, **5**, 421 (1891).

Stone, "The Quantitative Determination of Carbohydrates in Foodstuffs," *J. Am. Chem. Soc.*, **19**, 183 (1897).

Stone and Tollens, "Über Bildung von Furfurol und Nichtbildung von Lävulinsäure aus Arabinose. Furfurolbildung ist eine Reaction auf Arabinose," *Ann.*, **249**, 227 (1888).

Swartz, "Nutritional Investigations on the Carbohydrates of Lichens, Algae, and Related Substances. The Nutritive Value of Seaweeds," *Trans. Conn. Acad. Arts. Sci.*, **16**, 247 (1911); abstracted in *C. A.*, **7**, 1744 (1913).

Testoni, "Quantitative colorimetrische Bestimmung der Pentosane in Mehler," *Staz. sper. agrar. ital.*, **50**, 97 (1917); abstracted in *Chem. Zentr.*, **89** II, 865 (1918).

Tollens, "Untersuchungen über Kohlenhydrate," *Landw. Vers.-Stat.*, **39**, 401 (1891).

Tollens, "Nachtrag zu der Abhandlung von Mann, Krüger, und Tollens über Bestimmung der Pentosen und Pentosane durch Furfuroldestillation," *Z. angew. Chem.*, **9**, 194 (1896).

Tollens, "Über die Bestimmung der Pentosen und Pentosane, mit Kröber's Tabelle in Anhange," *Z. physiol. Chem.*, **36**, 239 (1902).

Tollens, "Quantitative Bestimmung der Glukuronsäure im Urin mit der Furfurol-Salzsäuredestillationsmethode," *Z. physiol. Chem.*, **61**, 95 (1909).

Tolman and Trescott, "A Study of the Methods for the Determination of Esters, Aldehydes, and Furfural in Whisky," *J. Am. Chem. Soc.*, **28**, 1619 (1906).

Treadwell and Hall, "Analytical Chemistry," Vol. II, **1919**, p. 268. John Wiley & Sons, Inc., New York.

Unger and Jäger, "Über Pentosanbestimmung," *Ber.*, **36**, 1222 (1903).

Van Ekenstein and Blanksma, "Über das ω-Oxymethylfurfurol als Ursache einiger Farbreaktionen der Hexosen," *Ber.*, **43**, 2355 (1910).

Van Haarst and Olivier, "Determination of Pentosans," *Chem. Weekblad*, **11**, 918 (1914); abstracted in *C. A.*, **10**, 28 (1916).

Vignon, "Osazones Oxycellulosiques," *Bull. soc. chim.*, **21**, 600 (1899).

Völckel, "Fortgestzte Untersuchungen über die Producte der trockenen Destillation organischer Körper," *Ann.*, **86**, 59 (1853).

Votocek, "Condensation des Methylfurols mit Phloroglucin," *Ber.*, **30**, 1195 (1897).

Votocek and Potmesil, "Über die Quantitative Bestimmung des Phloroglucins und des Resorcins mittels Furfurol," *Ber.*, **49**, 1185 (1916).

Walton, "The Preparation of Rhamnose," *J. Am. Chem. Soc.*, **43**, 127 (1921).

Wedekind, "Heterocyklische Verbindungen," **1901**, p. 26. Veit und Comp., Leipzig.

Welbel and Zeisel, "Über die Condensation von Furfurol mit Phloroglucin und eine auf diese gegründete Methode der quantitativen Bestimmung des Furfurols aus Pentosen und Pentosanen," *Monatsch.*, **16**, 283 (1895).

Wenzel and Lazar, "Über die Phloroglucinreaktion der Pentosen," *Monatsch.*, **34**, 1942 (1913).

Wheeler and Tollens, "Über die Xylose oder den Holzzucker, eine zweite Pentaglycose," *Ann.*, **254**, 304 (1889).

Wheeler and Tollens, "Untersuchungen über das Holzgummi," *Ann.*, **254**, 320 (1889).

Wichter and Tollens, "Pentosans of Certain Wood Fungi," *J. Landw.*, **58**, 238 (1911); abstracted in *Analyst*, **36**, 162 (1911).

Widtsoe and Tollens, "Über die Reactionen des Methylfurfurols und der Methylpentosane," *Ber.*, **33**, 143 (1900).

BIOGRAPHICAL

Norville Clarence Pervier was born February 26, 1891 at Clinton, Iowa. He attended public school and high school at Cedar Rapids, Iowa, graduating from high school in 1909. He entered Iowa State College in the fall of 1910 and was graduated in June, 1916 with the degree of B.S. in Applied Chemistry, having spent two intervening years teaching manual training in the public schools at Mountain Lake, Minnesota. He was registered in the Graduate Division of Iowa State College in January, 1916, and received the degree of M.S. in Physiologic Chemistry at that institution in June, 1917, his thesis being "The Determination of Creatine and Creatinine in Urines."

He was awarded a teaching fellowship at Iowa State College for the academic year 1916–17 and was appointed instructor there for the year 1918–19. He was appointed instructor at the University of Minnesota in September, 1920.

In 1917 and again in 1919–20 he was employed by the Standard Chemical Company, Des Moines, Iowa, in the capacity of chemist and assistant factory superintendent.

He entered the U. S. Army in February, 1918, and, after spending four months in training at Camp Dodge, was transferred to the Rockefeller Institute for Medical Research, where he was made sergeant in September, 1918. From there he was ordered to Yale University and on November 15, 1918 was granted an indefinite furlough in order to teach Chemistry at Iowa State College. He was finally ordered to Camp Dodge and given honorable discharge from the army in January, 1919.

In May, 1922, he presented to the faculty of the Graduate School of the University of Minnesota a thesis on "The Estimation of Pentoses and Pentosans" in partial fulfillment of the requirements for the degree of Doctor of Philosophy. The degree was conferred June 14, 1922.

He published in coöperation with Mr. G. P. Plaisance an article on "A Simple Device for Evaporating Solutions to a Definite Volume" in the Journal of the American Chemical Society in June, 1917.

He is a member of the following societies, American Chemical Society, Phi Lambda Upsilon, Sigma Xi, and Alpha Chi Sigma.

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